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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant: Masanori NAKAMURA et al.  
Title: EXHAUST GAS PURIFYING CATALYST AND METHOD OF  
PRODUCING SAME  
Appl. No.: 09/985,793  
Filing Date: November 6, 2001  
Examiner: W. Wright  
Art Unit: 1754

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**ENGLISH TRANSLATION OF PRIORITY DOCUMENT**

Commissioner for Patents  
PO Box 1450  
Alexandria, Virginia 22313-1450

Sir:

Further to Applicants' claim of priority under 35 U.S.C. 119 from foreign application, Japanese Patent Application No. 2000-341458, filed November 11, 2000, Applicants submit herewith an English translation of said original foreign application, and a certificate from the translator of the accuracy of the translation.

Respectfully submitted,

Date January 22, 2004

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Serial No. 09/985,793

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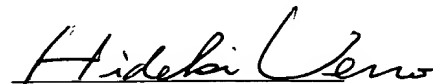
For: EXHAUST GAS PURIFYING CATALYST AND METHOD OF  
PRODUCING SAME

DECLARATION OF HIDEKI UENO

I, Hideki Ueno, residing at No. 3-17-5, Tsurumaki, Setagaya-ku, Tokyo, Japan, and working with ISP Corporation of No. 1-29, Akashi-cho, Chuo-ku, Tokyo, Japan, do hereby certify that I am fully conversant with the English and Japanese languages and, to the best of my knowledge and belief, the attached document is a true and accurate translation of a Japanese text for establishing an invention date. Both the translation and a copy of the Japanese text are attached hereto.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent resulting therefrom.

Date: January 16, 2004



Hideki Ueno

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Title of Invention EXHAUST GAS-PURIFYING CATALYST AND PRODUCING METHOD THEREFOR

Number of Claims 11

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[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION] EXHAUST GAS-PURIFYING CATALYST AND  
PRODUCING METHOD THEREFOR

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] An exhaust gas-purifying catalyst for  
adsorbing nitrogen oxide in exhaust gas from an internal  
combustion engine or fuel engine when the exhaust gas is in  
a lean region, and for reducing the adsorbed nitrogen oxide  
to nitrogen when the exhaust gas is in a rich region or  
stoichiometric region, characterized in

that the exhaust gas-purifying catalyst comprises, in  
a successively laminated manner:

a monolithic catalyst-carrier;

a catalytic layer (A) containing: at least one kind  
of noble metal selected from a group consisting of rhodium,  
platinum and palladium; at least one kind of compound  
selected from a group consisting of alkali metal compound,  
alkaline earth metal compound and rare earth metal  
compound; and alumina; and

a catalytic layer (B) containing: rhodium; platinum  
and/or palladium; at least one kind of compound selected  
from a group consisting of alkali metal compound, alkaline  
earth metal compound and rare earth metal compound; and  
alumina; and

that the content of the or each kind of compound  
selected from a group consisting of alkali metal compound,  
alkaline earth metal compound and rare earth metal compound  
of said catalytic layer (B), is larger than the content of

the or each compound of said catalytic layer (A).

[Claim 2] The exhaust gas-purifying catalyst of claim 1, characterized in

that the content ratio of the compound between said catalytic layer (B) and said catalytic layer (A) is between 1:1 exclusive and 3:1 inclusive.

[Claim 3] The exhaust gas-purifying catalyst of claim 1 or 2, characterized in

that the alumina content of each of said catalytic layers (A) and (B) is 100 g or more per 1 L of catalyst volume.

[Claim 4] The exhaust gas-purifying catalyst of any one of claims 1 through 3, characterized in

that the noble metal content per one piece catalyst-carrier is 1.5 to 3.0 g per 1 L of catalyst volume.

[Claim 5] The exhaust gas-purifying catalyst of any one of claims 1 through 4, characterized in

that the noble metal content per one piece catalyst-carrier is 1 to 50 g per 1 L of catalyst volume, in weight calculated as oxide.

[Claim 6] The exhaust gas-purifying catalyst of any one of claims 1 through 5, characterized in

that each of said catalytic layers (A) and (B) contains at least two kinds of compounds in the group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound.

[Claim 7] The exhaust gas-purifying catalyst of claim 6, characterized in

that the two kinds of compounds are barium compound and magnesium compound.

[Claim 8] An exhaust gas-purifying catalyst characterized in

that the exhaust gas-purifying catalyst comprises a monolithic catalyst-carrier coated with a catalytic layer containing:

at least one kind of noble metal selected from a group consisting of platinum, palladium and rhodium; at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound; and alumina; and

that the concentration difference of the or each compound between the inner section and surface section of the catalytic layer is within a range of  $\pm 10\%$ .

[Claim 9] A producing method of the exhaust gas-purifying catalyst of any one of claims 1 through 7, characterized in

that the method comprises the steps of:

coating, onto said monolithic catalyst-carrier, a slurry for said catalytic layer (A) obtained by grinding a mixture containing: a powder comprising alumina carrying thereon at least one kind of noble metal selected from a group consisting of rhodium, platinum and palladium; and an aqueous solution of at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound; and

further laminating, onto the above coated catalytic

layer (A), a slurry for said catalytic layer (B) obtained by grinding a mixture containing: a powder comprising alumina carrying thereon rhodium; a powder carrying thereon platinum and/or palladium; and an aqueous solution of at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound.

[Claim 10] The producing method of an exhaust gas-purifying catalyst of claim 9, characterized in

that the slurry for each of said catalytic layers (A) and (B) has a median diameter of 4  $\mu\text{m}$  or less.

[Claim 11] A producing method of the exhaust gas-purifying catalyst of claim 8, characterized in

that the method comprises the step of:

coating, onto said monolithic catalyst-carrier, a slurry for said catalytic layer obtained by grinding a mixture containing: a powder comprising alumina carrying thereon at least one kind of noble metal selected from a group consisting of platinum, palladium and rhodium; and an aqueous solution of at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound.

#### [DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of The Invention]

The present invention relates to: an exhaust gas-purifying catalyst and a producing method therefor, and particularly to an exhaust gas-purifying catalyst for



purifying hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NOx) in exhaust gas such as discharged from internal combustion engines of vehicles, boilers, and particularly for efficiently purifying NOx in exhaust gas in an oxygen-excessive region; and a method for producing such a catalyst.

[0002]

[Related Art]

There have been conventionally and eagerly desired vehicles of lower fuel cost such as in view of problems of exhaustion of petroleum resource and the global warming, and attention has been directed to development of lean-burn type vehicles among gasoline-fueled vehicles. In the lean-burn type vehicles, since the exhaust gas state is brought into an oxygen-excessive state (lean) during lean-burn running as compared with a stoichiometric air/fuel state, adoption of a usual three way catalyst in a lean region leads to a problem of an insufficient purifying action for nitrogen oxides (NOx) due to affection of excessive oxygen. This resulted in a demand for development of catalysts capable of purifying NOx even in an oxygen-excessive state.

[0003]

Such catalysts for purifying NOx in a lean region have been variously proposed, and there has been proposed a catalyst for purifying NOx by absorbing NOx in a lean region and releasing the NOx in a stoichiometric region, such as represented by a catalyst (JP-A-5-168860) comprising a porous carrier carrying platinum (Pt) and

lanthanum thereon.

However, sulfur (S) is contained in fuels and lubricants, and this sulfur is discharged as oxides in exhaust gas such that the NOx absorber is poisoned by sulfur, thereby causing a problem of a deteriorated NOx absorbing ability. This is called "poisoning with sulfur".

As a technique capable of avoiding such a poisoning with sulfur, the present inventors have already proposed a catalyst constituted to have, at its surface layer and inner layer, an S absorber (represented by magnesium (Mg)) for adsorbing sulfur and readily decomposing sulfur and an absorber (represented by barium (Ba)) for absorbing NOx, respectively, in Japanese Patent Application No. 2000-54825.

Further, JP-A-7-132226 has already disclosed such an invention to lower the concentrations of alkali metal and alkaline earth metal, in a gas flow direction from upstream to downstream.

[0004]

[Problems to be solved by the Invention]

However, there has been revealed the following possibility of improvement, after further investigations by the present inventors concerning the above techniques related to the present application.

Namely, it has been confirmed that, although the catalyst in the Japanese Patent Application No. 2000-54825 has a superior performance against the poisoning with sulfur, there is caused a slightly deteriorated performance

from a standpoint of adsorption of NOx.

Further, the JP-A-7-132226 completely fails to mention the poisoning with sulfur in its detailed description, and the present inventors have confirmed that the catalytic layers exhibit a higher effect against the poisoning with sulfur when the catalytic layers are laminated to each other.

Meanwhile, although JP-A-9-57099 presents a catalyst having a constitution substantially similar to the catalysts of the above-mentioned inventions, the using manner of this catalyst is fully different from the catalysts of the above-mentioned inventions.

[0005]

The present invention has been carried out in view of the conventional problems of the related art, and it is therefore an object of the present invention to provide: an exhaust gas-purifying catalyst for efficiently conducting absorption, release and purification of NOx while avoiding poisoning with sulfur; and a method for producing such a catalyst.

[0006]

[Means for Solving the Problem]

The present inventors have earnestly conducted investigations so as to solve the above problems and narrowly completed the present invention by resultingly discovering that the problems can be solved by producing a catalyst including laminated catalytic layers in a manner that compounds such as alkali metals are contained more in

the surface layer than in the inner layer and that the compounds such as alkali metals are mixed into a slurry or slurries for the catalyst.

[0007]

Namely, the present invention provides an exhaust gas-purifying catalyst for adsorbing nitrogen oxide in exhaust gas from an internal combustion engine or fuel engine when the exhaust gas is in a lean region, and for reducing the adsorbed nitrogen oxide to nitrogen when the exhaust gas is in a rich region or stoichiometric region, characterized in

that the exhaust gas-purifying catalyst comprises, in a successively laminated manner:

a catalytic layer (A) containing: at least one kind of noble metal selected from a group consisting of rhodium, platinum and palladium; at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound; and alumina; and

a catalytic layer (B) containing: rhodium; platinum and/or palladium; at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound; and alumina onto the monolithic catalyst-carrier

that the content of the or each kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound of the catalytic layer (B), is larger than the content of

the or each compound of the catalytic layer (A).

[0008]

Further, the exhaust gas-purifying catalyst of the present invention has a preferable configuration characterized in

that the content ratio of the compound between the catalytic layer (B) and the catalytic layer (A) is between 1:1 exclusive and 3:1 inclusive.

[0009]

Moreover, the present invention provides a producing method of the exhaust gas-purifying catalyst, characterized in

that the method comprises the steps of:

coating, onto the monolithic catalyst-carrier, a slurry for the catalytic layer (A) obtained by grinding a mixture containing: a powder comprising alumina carrying thereon at least one kind of noble metal selected from a group consisting of rhodium, platinum and palladium; and an aqueous solution of at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound; and

further laminating, onto the above coated catalytic layer (A), a slurry for the catalytic layer (B) obtained by grinding a mixture containing: a powder comprising alumina carrying thereon rhodium; a powder carrying thereon platinum and/or palladium; and an aqueous solution of at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and

rare earth metal compound.

[0010]

[Embodiments of the Invention]

The present invention will be explained hereinafter in detail. Note that the unit "%" used herein represents a mass percentage, unless otherwise specified.

The exhaust gas-purifying catalyst of the present invention is a so-called NO<sub>x</sub> adsorbing/reducing catalyst which: comprises a catalytic layer (A) and a catalytic layer (B) successively laminated onto the monolithic catalyst-carrier; and adsorbs nitrogen oxides in exhaust gas from an internal combustion engine or fuel engine when the exhaust gas is in a lean region and reduces the adsorbed nitrogen oxides into nitrogen in a rich region or stoichiometric region. Namely, there is adopted a constitution where the catalytic layer (A) and the catalytic layer (B) act as an inner layer and a surface layer, respectively. Contained in these catalytic layers are compounds of alkali metal, alkaline earth metal and/or rare earth metal acting as NO<sub>x</sub> and SO<sub>x</sub> absorbers.

[0011]

Exhaust gas contains sulfur oxide (SO<sub>x</sub>) in addition to NO<sub>x</sub>, and NO<sub>x</sub> has a lower adsorptive activity than SO<sub>x</sub>.

Thus, although the NO<sub>x</sub> and sulfur oxide (SO<sub>x</sub>) in the exhaust gas are adsorbed to the NO<sub>x</sub> adsorbing/reducing catalyst in the lean region, the NO<sub>x</sub> reaches not only the catalyst (B) at the surface layer but also the catalyst (A) at the inner layer.

On the other hand, most of the SOx is adsorbed to the surface layer and does not reach the inner layer. This results in a state where NOx and SOx are adsorbed in the surface layer of the catalyst, and NOx is adsorbed in the inner layer.

The adsorbed NOx and SOx are released from the catalyst, when the exhaust gas is brought into a rich region or stoichiometric region. At this time, while the NOx is released from the surface layer and inner layer, the SOx is released from the surface layer and rarely from the inner layer.

[0012]

Further, in order that the adsorbed SOx is released from the catalyst, there is required a large amount of reducing agent. While the main reducing agent exemplarily includes HC, CO within the exhaust gas, the amount of these reducing gases deeply reaching the inner layer of the catalyst is assumed to be so small that the SOx, if any, adsorbed in the inner layer is rarely released.

[0013]

Thus, if SOx is adsorbed in the surface layer as much as possible without allowing the SOx to reach the inner layer when the exhaust gas is in the lean region, the SOx can be readily released in the rich region or stoichiometric region.

The exhaust gas-purifying catalyst of the present invention contains compounds of alkali metal, alkaline earth metal and/or rare earth metal acting as NOx and SOx

absorbers, and the content of compound(s) of the catalytic layer (B) as the surface layer is larger than that of the catalytic layer (A) as the inner layer, thereby allowing the SOx to be efficiently adsorbed to the surface layer. Further, since the adsorbed SOx can be readily released, poisoning with sulfur can be prevented and NOx can be efficiently purified even in a lean region without deteriorating the NOx absorbing ability.

[0014]

In this respect, if a single catalyst-carrier are exemplarily and dividedly coated with a catalyst having a larger content of compound(s) such as the above-mentioned alkali metal compound at an upstream side and coated with another catalyst having a smaller content of compound(s) at a downstream side concerning the exhaust gas, SOx which has not been adsorbed at the upstream side catalyst is obliged to flow into the downstream side catalyst if the upstream side catalyst fails to sufficiently adsorb the SOx, thereby failing to efficiently adsorb and release the SOx and thus causing poisoning with sulfur. There is a further problem that the SOx released at the upstream side is again adhered to the downstream side catalyst.

Nonetheless, the exhaust gas-purifying catalyst of the present invention adopts such a laminated structure that the surface layer comprises the catalyst having a larger content of compound(s) of alkali metal and the like, thereby avoiding poisoning with sulfur.

[0015]



While the catalytic layer (B) contains the compound(s) of alkali metal and the like at a content in a larger amount than the (A), the content ratio between the catalytic layers (B) and (A) is to be preferably between 1:1 exclusive and 3:1 inclusive.

Content ratios of 1:1 or less fail to sufficiently obtain an effect for avoiding the poisoning with sulfur and for keeping the NO<sub>x</sub> absorbing ability from being deteriorated, while increased amounts of the compound(s) of alkali metal and the like exceeding 3:1 may lead to an increased thermal degradation of noble metal(s) contained in the catalytic layer (B) as the surface layer.

[0016]

Further, the content of compound(s) of alkali metal and the like per one piece catalyst-carrier is preferably 1 to 50 g per 1 L of catalyst volume, in weight calculated as oxide. Contents less than 1 g fail to sufficiently obtain an effect of the compound(s) of alkali metal and the like for absorbing NO<sub>x</sub> and SO<sub>x</sub>, while contents exceeding 50 g fail to obtain a meaningful effect corresponding to the increased amount and may rather promote the thermal degradation of the noble metal such as Rh, Pt.

[0017]

The compound(s) of alkali metal and the like is/are not particularly limited, insofar as comprising compound(s) based on alkali metal, alkaline earth metal or rare earth metal or any combination thereof. Concretely, the metal(s) preferably includes sodium (Na), potassium (K), rubidium

(Rb), cesium (Cs), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), lanthanum (La), praseodymium (Pr), neodymium (Nd). The compound(s) are preferably in the form(s) of carbonate, oxide and hydroxide.

Inclusion of two kinds of these compounds into the catalytic layers (A) and (B) enhances the SO<sub>x</sub> absorbing and releasing effects. This is assumed to be caused by the fact that the two kinds of the compounds of alkali metal and the like are made complex, such that the decomposition of sulfate compound is promoted, thereby allowing SO<sub>x</sub> to be readily released even when such a sulfate compound is generated due to poisoning with sulfur.

The above effect is particularly enhanced in case of combining compounds of barium (Ba) and magnesium (Mg), and this is also proven by a formation of compound BaMg(CO<sub>3</sub>)<sub>2</sub> based on XRD (X-ray diffraction analysis).

[0018]

In addition to the above compound(s) of alkali metal and the like, the catalytic layer (A) contains noble metal(s) comprising rhodium (Rh), platinum (Pt) or palladium (Pd) or an arbitrary combination thereof as well as alumina, while the catalytic layer (B) contains: Rh; Pt and/or Pd; and alumina.

While the noble metal(s) such as Rh contained in the catalytic layers (A) and (B) plays a role of a so-called three-way purifying function, the NO<sub>x</sub> and SO<sub>x</sub> purifying efficiencies are further improved in the present invention by particularly containing Rh in the catalytic layer (B) as

the surface layer.

[0019]

Further, the contents of alumina in the catalytic layers (A) and (B) are preferably 100 g per 1 L of catalyst volume, respectively. At contents less than 100 g, the compounds of alkali metal and the like are closely contacted with each other and thus tend to aggregate, thereby possibly failing to obtain a sufficient effect as the NO<sub>x</sub> and SO<sub>x</sub> absorbers.

[0020]

It is also preferable that the content of the above noble metal(s) per one piece catalyst-carrier is 1.5 to 3.0 g inclusive per 1 L of catalyst volume. Such a relatively small amount of noble metal(s) rather causes SO<sub>x</sub> to be efficiently adsorbed and released.

The noble metal(s) less than 1.5 g leads to an increased thermal degradation of the noble metal(s), while the noble metal(s) exceeding 3.0 g leads to adsorption of SO<sub>x</sub> more than necessary such that the adsorption can not be fully carried out only by the surface layer and SO<sub>x</sub> deeply reaches the inner layer thereby complicating the release of SO<sub>x</sub>.

[0021]

The exhaust gas-purifying catalyst of the present invention can improve the efficiency of NO<sub>x</sub> adsorption and NO<sub>x</sub> release and purification and can avoid poisoning with sulfur, even in a constitution of a monolithic catalyst-carrier coated thereon with a catalytic layer containing:

noble metal(s) comprising Pt, Pd or Rh or an arbitrary combination thereof; compound(s) based on alkali metal, alkaline earth metal or rare earth metal or any combination thereof; and alumina.

[0022]

In this case, the compound(s) of alkali metal and the like is preferably uniformly and highly dispersed in the catalytic layer, and concretely, the concentration difference of the compound(s) of alkali metal and the like between the inner section and surface section of the catalytic layer is preferably within a range of  $\pm 10\%$ .

This concentration difference can be specified by such an analyzing method utilizing an XMA (X-ray microanalyzer). In a typical case of a catalytic layer having a thickness of 60  $\mu\text{m}$ , it is possible to obtain the concentration difference by measuring the compound concentration at the outermost surface of the catalytic layer and the compound concentration at the depth of 30  $\mu\text{m}$  from the outermost surface. Note that the thickness of the catalytic layer does not refer to a thickness of a corner portion of a honeycomb carrier but refers to a thickness of a flat portion of the carrier, as shown in FIG. 1.

The compounds of alkali metal and the like are thus uniformly carried within the catalytic layer, and highly dispersed within the catalytic layer. As a result, there are exhibited and efficiently promoted such reactions that:  $\text{NO}_x$  is adsorbed as  $\text{NO}_2$  into the catalytic layer when the amount of reducing gas (HC, CO and  $\text{NO}_x$ ) is decreased

relative to the amount of oxidizing gas ( $O_2$  and  $NO_x$ ), while the adsorbed  $NO_2$  is conversely released and purified when the amount of reducing gas is increased relative to the amount of oxidizing gas. Further, S tends to be readily desorbed by virtue of the reducing gas, even when the S has adhered to the catalytic layer. This is assumed to be caused by the fact that the compounds of alkali metal and the like are carried within the catalytic layer in a higher dispersed state so that the S desorbing rate by the reducing gas is increased.

[0023]

Note that while the contents of alumina, noble metal(s) and compound(s) of alkali metal and the like as well as the kinds of compounds are not particularly limited in this exhaust gas-purifying catalyst of the present invention, there can be obtained a higher effect in case of adopting the same contents and kinds as those in the other exhaust gas-purifying catalyst of the present invention.

[0024]

Further, these exhaust gas-purifying catalysts of the present invention desirably have higher heat resistance, also in view of situations where the catalysts are subjected to high temperatures. It is thus possible to add increased amounts of the materials for improving heat resistance such as noble metal(s) or alumina, as components of the catalytic layer(s). Such materials exemplarily include ceria, zirconia, lanthanum and barium which have been conventionally used in a three-way catalyst.

While the monolithic catalyst-carrier can be appropriately selected from known catalyst-carriers and used, there is typically used a carrier comprising a refractory inorganic material.

Moreover, while the shape of the catalyst-carrier is not particularly limited, it is preferable to employ a honeycomb structural body such as constituted of cordierite, stainless steel and to use the structural body by coating thereon the powders for the above catalytic layers. It is further possible to form the catalytic powders themselves into a honeycomb shape.

Note that NO<sub>x</sub> can be efficiently purified in the exhaust gas-purifying catalyst of the present invention, when the operating air/fuel ratio is within a range of 20 to 50 and a range of 10.0 to 14.6.

[0025]

There will be explained hereinafter the producing method of the exhaust gas-purifying catalysts of the present invention.

The producing method of the exhaust gas-purifying catalysts of the present invention is to mix: a powder comprising alumina carrying thereon noble metal(s) comprising Pt, Pd or Rh or an arbitrary combination thereof; with an aqueous solution of compound(s) based on alkali metal, alkaline earth metal or rare earth metal or any combination thereof. This mixture is ground into a slurry for the catalytic layer (A), and this slurry is coated onto a monolithic catalyst-carrier.

Next, there are mutually mixed: a powder comprising alumina carrying thereon Rh; a powder carrying thereon Pt and/or Pd; and an aqueous solution of compound(s) based on alkali metal, alkaline earth metal or rare earth metal or any combination thereof. This mixture is ground into a slurry for the catalytic layer (B), and this slurry is further laminated onto the coated catalytic layer (A).

Note that the mixtures may contain other catalytic components such as materials for improving the heat resistance, as noted above.

[0026]

While various techniques have been adopted in the conventional producing methods so as to carry compound(s) of alkali metal and the like on catalytic components, representative one of such techniques is to coat a slurry such as containing alumina carrying thereon noble metal(s) or the like, onto a catalyst-carrier, and then to immerse the catalyst-carrier in an aqueous solution containing alkali metal or the like.

In the producing method of the present invention, since the alumina carrying thereon noble metal(s) and the aqueous solution of compounds of alkali metal and the like are mixed together and then ground such that the particle size of the compound(s) of alkali metal and the like is decreased, sulfate compound tends to be readily decomposed even when such sulfate compound is generated by poisoning with sulfur due to adsorption of S to the catalytic layers (A) and (B). Further, NO<sub>x</sub> can be efficiently absorbed and

desorbed, even if the amount of noble metal(s) contained in the catalyst is relatively small as described above.

Although the particle size of compound(s) of alkali metal and the like in the catalyst produced by the producing method of the present invention was confirmed to be 22 nm by XRD, the particle size was 27 nm in case of a catalyst produced by forming a catalytic layer on a catalyst-carrier and by subsequently impregnating a solution of alkali metal and the like into the catalyst-carrier.

[0027]

The slurry is to preferably have a median diameter of 4  $\mu\text{m}$  or less. This decreases the particle size of the compound(s) of alkali metal and the like, thereby further promoting the effect that the sulfate compound generated due to poisoning with sulfur tends to be readily decomposed.

[0028]

Further, to substantially uniformly and highly disperse the compound(s) of alkali metal and the like in the catalytic layer such that the concentration difference of the compound(s) of alkali metal and the like between the inner section and surface section of the catalytic layer is kept within a range of  $\pm 10\%$ , it is advisable to: prepare a slurry by grinding a mixture of a powder comprising alumina carrying thereon noble metal(s) comprising Pt, Pd or Rh or an arbitrary combination thereof, and an aqueous solution of compound(s) based on alkali metal, alkaline earth metal or rare earth metal or any combination thereof; and coat



the slurry onto a monolithic catalyst-carrier; similarly to the above producing method.

According to such a producing method, the compound(s) of alkali metal and the like can be carried on other catalytic components in a well dispersed state, thereby increasing an S desorbing rate of the catalyst with the aid of the reducing gas, while allowing: avoidance of poisoning with sulfur; and maintenance of efficiencies for adsorbing, releasing and purifying NOx.

[0029]

[Examples]

The present invention is explained hereinafter in more detail based on Examples and Comparative Examples, and the present invention is not limited to these Examples.

[0030]

(Example 1)

Alumina was impregnated with an aqueous solution of dinitrodiammine Pt, and then calcined in air at 400 °C for 1 hour after drying, thereby obtaining Pt-carrying alumina powder (Powder a). This powder had a Pt concentration of 1.0 %.

Next, the Powder a, alumina, a solution of Ba acetate and water were charged into a porcelain ball mill, and mixed and ground therein, thereby obtaining a slurry. This slurry had a median diameter of 3  $\mu\text{m}$ . This slurry was coated onto a monolithic cordierite carrier (1.7 L, 400 cells), the excessive slurry within the cells was removed by airflow, and the carrier was dried at 130 °C and then

calcined at 400 °C for 1 hour, thereby forming a catalytic layer (A) of 110g/L.

[0031]

Further, alumina was impregnated with an aqueous solution of dinitrodiammine Pt, and then calcined in air at 400 °C for 1 hour after drying, thereby obtaining Pt-carrying alumina powder (Powder b). This powder had a Pt concentration of 1.5 %.

Moreover, alumina was impregnated with an aqueous solution of Rh nitrate, and then calcined in air at 400 °C for 1 hour after drying, thereby obtaining Rh-carrying alumina powder (Powder c). This powder had an Rh concentration of 2.0 %.

Next, the Powder b, Powder c, alumina, a solution of Ba acetate and water were charged into a porcelain ball mill, and mixed and ground therein, thereby obtaining a slurry. This slurry had a median diameter of 3  $\mu\text{m}$ . This slurry was coated onto the catalytic layer (A), the excessive slurry within the cells was removed by airflow, and the carrier was dried at 130 °C and then calcined at 400 °C for 1 hour, so as to form a catalytic layer (B) of 120 g/L, thereby obtaining the catalyst of this Example.

This catalyst contained Pt=2.0 g/L, Rh=0.5 g/L, and Ba (calculated as oxide)=30 g/L. Further, Ba was contained such that catalytic layer (B): catalytic layer (A)=2:1.

[0032]

(Example 2)

The catalyst of this Example was obtained by

repeating the procedure for the Example 1, except that: the slurry for the catalytic layer (A) was obtained by charging the Powder a, alumina, the solution of Ba acetate, a solution of Mg acetate tetrahydrate and water into a porcelain ball mill, and mixing and grinding them, while the slurry for the catalytic layer (B) was obtained by charging the Powder b, Powder c, alumina, the solution of Ba acetate, the solution of Mg acetate tetrahydrate and water into the porcelain ball mill, and mixing and grinding them.

This catalyst contained Pt=2.0 g/L, Rh=0.5 g/L, Ba (calculated as oxide)=20 g/L, and Mg (calculated as oxide)=10 g/L. Further, Ba and Mg were contained such that catalytic layer (B): catalytic layer (A)=2:1.

[0033]

(Comparative Example 1)

The Powder a, alumina and water were charged into a porcelain ball mill, and mixed and ground to thereby obtain a slurry, and this slurry was coated onto a monolithic cordierite carrier which was then dried and calcined under the same conditions as the Example 1 to thereby form a catalytic layer of 100 g/L, followed by impregnation of an aqueous solution of Ba acetate into the catalytic layer thereby forming a catalytic layer (C) of 110 g/L.

Next, the Powder b, Powder c, alumina and water were charged into a porcelain ball mill, and mixed and ground to thereby obtain a slurry which was then coated onto the catalytic layer, followed by drying and calcining under the

same conditions as the Example 1, thereby further laminating a catalytic layer of 100 g/L. This was impregnated with an aqueous solution of Ba acetate to form a catalytic layer (D), thereby obtaining the catalyst of this Comparative Example.

This catalyst contained Pt=2.0 g/L, Rh=0.5 g/L, and Ba (calculated as oxide)=30 g/L. Further, Ba was contained such that catalytic layer (D): catalytic layer (C)=2:1.

[0034]

(Comparative Example 2)

The Powder b, Powder c, alumina, the solution of Ba acetate and water were charged into a porcelain ball mill, and mixed and ground, thereby obtaining a slurry. This slurry had a median diameter of 3  $\mu$ m. This slurry was coated onto a monolithic cordierite carrier (1.7 L, 400 cells), the excessive slurry within the cells was removed by airflow, and the carrier was dried at 130 °C and then calcined at 400 °C for 1 hour, thereby obtaining a Catalyst 1 having a catalytic layer of 120g/L.

This Catalyst 1 contained Pt=1.0 g/L, Rh=0.5 g/L, and Ba (calculated as oxide)=20 g/L.

[0035]

The Powder a, the solution of Ba acetate and water were charged into a porcelain ball mill, and mixed and ground, thereby obtaining a slurry. This slurry had a median diameter of 3  $\mu$ m. This slurry was coated onto a monolithic cordierite carrier (1.7 L, 400 cells), the excessive slurry within the cells was removed by airflow,

and the carrier was dried at 130 °C and then calcined at 400 °C for 1 hour, thereby obtaining a Catalyst 2 having a catalytic layer of 110g/L.

This Catalyst 2 contained Pt=1.0 g/L, and Ba (calculated as oxide)=10 g/L.

These catalysts were arranged in series, in an order of the Catalyst 1 and Catalyst 2 from the upstream side relative to an exhaust gas flowing direction.

[0036]

(Comparative Example 3)

The catalyst of this Comparative Example was obtained by repeating the procedure for the Example 1, except that: the catalytic layer (B) and catalytic layer (A) were laminated at 90 g/L and 80 g/L, respectively.

[0037]

(Comparative Example 4)

The catalyst of this Comparative Example was obtained by repeating the procedure for the Example 1, except that: the median diameter of each of the slurries for the catalytic layers (A) and (B) was 5  $\mu\text{m}$ .

[0038]

(Comparative Example 5)

The catalyst of this Comparative Example was obtained by repeating the procedure for the Example 1, except that: the catalyst contained Ba (calculated as oxide)=60 g/L.

[0039]

<Endurance Test>

Each of the catalysts of the Examples and Comparative

Examples was installed in an exhaust system of an engine having a displacement of 4,400 cc while using a domestic regular gasoline and setting a catalyst inlet temperature at 650 °C, and the engine was operated for 50 hours.

There were subsequently conducted an S poisoning treatment (by using a gasoline having an S concentration of 300 ppm, setting the catalyst inlet temperature at 350 °C, and operating the engine for 5 hours), and an S desorbing treatment (by using a domestic regular gasoline, setting the catalyst inlet temperature at 650 °C, and operating the engine for 30 minutes).

[0040]

<Evaluation Test>

Each of the catalysts of the Examples and Comparative Examples was installed in an exhaust system of an engine having a displacement of 2,000 cc, and the engine was operated in a manner of lean (A/F=20) for 10 seconds→rich (A/F=11.0) for 2 seconds→stoichiometric (A/F=14.7) for 5 seconds, thereby obtaining an exhaust gas purifying ratio during this period. The inlet temperature was set at 350 °C.

The test result is shown in Table 1.

[0041]

[Table 1]

Conversion Ratio

	After Endurance	After S Desorbing Treatment
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	HC	CO	NOx	HC	CO	NOx
Example 1	95	95	80	97	96	75
Example 2	97	98	85	98	98	82
Com. Ex. 1	95	95	78	96	96	63
Com. Ex. 2	95	95	75	95	95	58
Com. Ex. 3	95	94	70	95	95	41
Com. Ex. 4	95	95	78	96	96	68
Com. Ex. 5	93	93	78	95	95	44

[0042]

(Example 3)

Alumina was impregnated with an aqueous solution of dinitrodiammine Pt, and then calcined in air at 400 °C for 1 hour after drying, thereby obtaining Pt-carrying alumina powder (Powder d). This powder had a Pt concentration of 1.0 %.

Boehmite alumina was impregnated with an aqueous solution of Rh nitrate, and then calcined in air at 400 °C for 1 hour after drying, thereby obtaining an Rh-carrying boehmite alumina powder (Powder e). This powder had an Rh concentration of 1.0 %.

[0043]

The Powder d, Powder e, an alumina powder and the solution of Ba acetate were charged into a porcelain ball mill, and mixed and ground, thereby obtaining a slurry. This slurry was coated onto a monolithic cordierite carrier (1.7 L, 400 cells), the excessive slurry within the cells was removed by airflow, and the carrier was dried at 130 °C

and then calcined at 400 °C for 1 hour, thereby obtaining a catalyst having a catalytic layer of 100 g/L. This procedure was conducted again to additionally coat 130 g/L, thereby obtaining a catalyst of 230 g/L of this Example.

This catalyst contained Pt=2.0 g/L, Rh=0.5 g/L, and Ba (calculated as oxide)=30 g/L. Further, the surface-inside concentration difference was within a range of  $\pm 10$  % in each of the firstly and secondly coated layers, as a result of inspection of distribution of Ba within the catalytic layer by XMA.

[0044]

(Comparative Example 6)

There was prepared a slurry equivalent to the slurry of the Example 1 while excluding the solution of Ba acetate therefrom, and this slurry was coated onto a catalyst-carrier, thereby obtaining a catalyst having a catalytic layer of 100 g/L. This procedure was conducted again to additionally coat 100 g/L, thereby obtaining a catalyst of 200 g/L of this Example. This catalyst was impregnated with an aqueous solution of Ba acetate, thereby obtaining a catalyst having a catalytic layer of 230 g/L of this Example.

This catalyst contained Pt=2.0 g/L, Rh=0.5 g/L, and Ba (calculated as oxide)=30 g/L. Further, the surface-inside concentration difference, i.e., the concentration difference of the inner section relative to that of the surface section of the firstly coated layer was about +10 %, and so was about +15 % for the secondly coated layer, as a



result of inspection of distribution of Ba within the catalytic layers by XMA.

[0045]

(Example 4)

There was obtained a catalyst of this Example by repeating the same procedure as the Example 1, except for addition of Mg acetate to the slurry of the Example 1.

This catalyst contained Pt=2.0 g/L, Rh=0.5 g/L, Ba (calculated as oxide)=20 g/L, and Mg (calculated as oxide)=10 g/L. Further, the surface-inside concentration differences of Ba and Mg were within a range of  $\pm 10\%$  in each of the firstly and secondly coated layers, as a result of inspection of distributions of Ba and Mg within the catalytic layer by XMA.

[0046]

<Endurance Test and Evaluation Test>

There were conducted the same procedures as the above endurance test and evaluation test.

The test result is shown in Table 2.

[0047]

[Table 2]

Conversion Ratio (%)

	Conversion Ratio		
	CO	HC	NOx
Example 1	99	90	92
Com. Ex. 1	98	90	85
Example 2	98	91	95

[0048]

[Effect of the Invention]

According to the present invention as explained above, the compound(s) of alkali metal and the like is contained more in the surface layer than in the inner layer of the laminated catalytic layers while producing the catalyst by mixing the compound(s) of alkali metal and the like in the slurry for the catalyst: thereby allowing provision of an exhaust gas-purifying catalyst for efficiently conducting absorption, release and purification of NO<sub>x</sub> while avoiding poisoning with sulfur; and provision of a producing method for such a catalyst.

[BRIEF DESCRIPTION OF THE DRAWING]

[FIG. 1]

A cross-sectional view showing catalytic layers of an exhaust gas-purifying catalyst of the present invention coated on a cell.

[NAME OF DOCUMENT] Abstract

[ABSTRACT]

[OBJECT] To provide: an exhaust gas-purifying catalyst for efficiently conducting absorption, release and purification of NOx while avoiding poisoning with sulfur; and a producing method for such a catalyst.

[CONSTITUTION] An exhaust gas-purifying catalyst, comprising, in a successively laminated manner:

a monolithic catalyst-carrier;

a catalytic layer (A) containing: at least one kind of noble metal selected from a group consisting of Rh, Pt and Pd; at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound; and alumina; and

a catalytic layer (B) containing: Rh; Pt and/or Pd; at least one kind of compound selected from a group consisting of alkali metal compound, alkaline earth metal compound and rare earth metal compound; and alumina; and

wherein the content of the or each compound of the catalytic layer (B) is larger than the content of the or each compound of the catalytic layer (A).

[SELECTED DRAWING] None



FIG. 1

[ハニカム担体] Honeycomb Carrier

[(セル)] (Cell )

[触媒層] Catalytic Layer



FIG. 1

